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HYDROSILYLATION OF THE $C\equiv C$ TRIPLE BOND BY PHENYL- AND THIENYL-SILANES *

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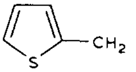
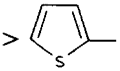
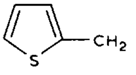
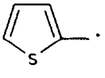
Summary

The effects of the structures of the hydrosilane and the acetylene derivative, catalyst, temperature and solvent on the yields and ratio of isomers during the hydrosilylation of phenylacetylene, 2-(ethynyl)thiophene, 2-(propargyl)thiophene, methyl propiolate, propargyl alcohol and its methyl ether, and propargyl amines by phenyl- and thienyl-hydrosilanes have been studied. The yields of the reaction products upon hydrosilylation of $HC\equiv CX$ compounds by dimethyl(2-thienyl)silane in the presence of chloroplatinic acid at 50°C decrease in the following sequence of substituents X: COOMe ≈  $\geqslant$ $HOCH_2$ > Ph > $MeOCH_2$ >  > R_2NCH_2, but the amount of the β-isomer diminishes in the order: R_2NCH_2 >  $\geqslant$ Ph > $MeOCH_2$ > $HOCH_2$ > COOMe > .

Introduction

Thienylhydrosilanes are highly reactive in the hydrosilylation of allyl amines [1,2], allyl- and vinyltrialkylsilanes [3], and vinylsilatrane [4]. The hydrosilylation of the triple bond has not been examined; the literature cites only a single example of propargyl alcohol hydrosilylation by methyldi(2-thienyl)silane [5]. In this connection, we have investigated the reaction of phenylacetylene, 2-(ethynyl)thiophene, 2-(propargyl)thiophene, methyl propiolate, propargyl alcohol and its methyl ether, and propargyl amines with phenyl- and 2-thienyl-silanes.

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* Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on 5 September, 1985.

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Results and discussion

The hydrosilylation of acetylene derivatives by arylhydrosilanes in the presence of chloroplatinic acid leads, in most cases, to two products, viz. *β-trans*- and α-isomers.

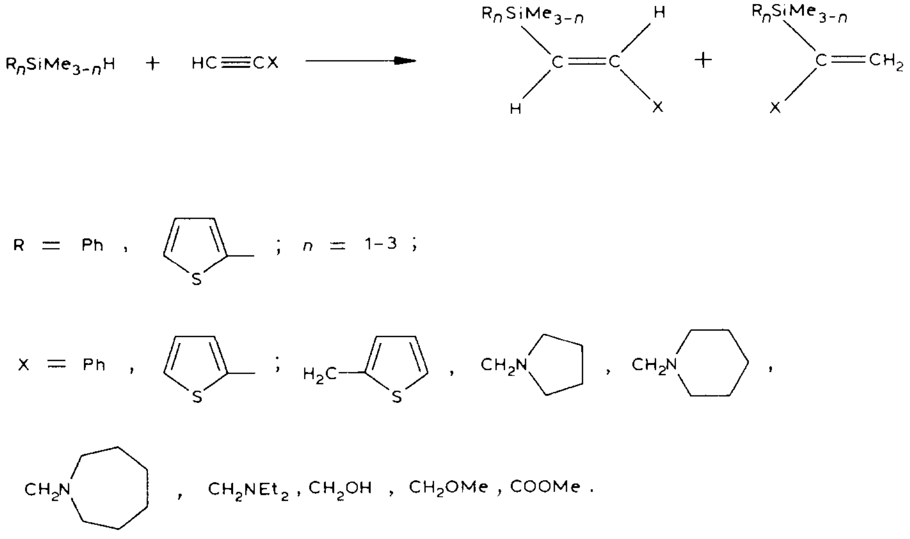


TABLE 1

HYDROSILYLATION OF PHENYLACETYLENE AND 2-(ETHYNYL)THIOPHENE* BY ARYLHYDROSILANES $Ar_nSiMe_{3-n}H$ ($H_2PtCl_6 \cdot 6H_2O$, 50°C, 6 h)

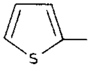
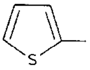
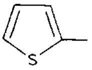
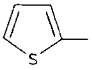
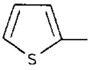
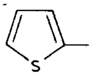
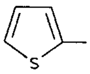
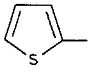
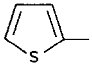
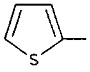
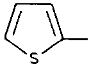
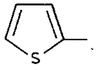
Ar	*n*	Yield (%)	*β-trans*/α-isomer ratio
	1	89	73/27
	1	64*	30/70
	2	89	71/29
	2	.17*	50/50
	3	67	70/30
Ph	1	79	69/31
Ph	2	91	78/22
Ph	3	86	90/10

TABLE 2

HYDROSILYLATION OF 2-(PROPARGYL)THIOPHENE BY ARYLHYDROSILANES $Ar_nSiMe_{3-n}H$ ($H_2PtCl_6 \cdot 6H_2O$, 6 h)

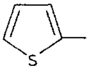
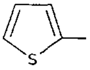
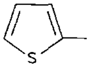
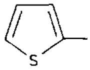
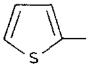
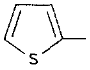
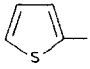
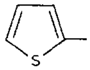
Ar	*n*	*T* (°C)	Yield (%)	β-*trans*/α-isomer ratio
	1	150	87	64/36
	2	150	82	70/30
	3	150	82	77/23
	1	50	98	75/25
	2	50	82	73/27
	3	50	91	83/17
	1	20	80	72/28
Ph	1	50	74	84/16
Ph	2	50	72	75/25
Ph	3	50	46	81/19

The reaction of phenylacetylene with phenyl- and thienyl-hydrosilanes in the presence of Speier's catalyst occurs easily (70–90% yield) at 50°C, the β-*trans*-isomer being predominantly formed (Table 1). At the same time, the hydrosilylation of 2-(ethynyl)thiophene by dimethyl(2-thienyl)- and methyldi(2-thienyl)-silanes under the same conditions is characterized by 64% and 17% yields, respectively. The reaction fails to occur in the case of tri(2-thienyl)silane at 50 and 150°C. The ratio of the α- and β-*trans*-isomers formed in the reaction of 2-(ethynyl)thiophene with dimethyl(2-thienyl)silane is 70/30, whereas the hydrosilylation of phenylacetylene leads to the reverse situation (β-*trans*/α-isomer ratio is 73/27). This is apparently due to the greater inductive electron-acceptor effect of the 2-thienyl group ($\sigma^* = +1.3$), as compared to the phenyl one ($\sigma^*_{Ph} = +0.6$). Incorporation of a methylene group between the thiophene ring and the C≡C triple bond increases the yields of the hydrosilylation products, the β-*trans*-isomer being predominant (Table 2).

The hydrosilylation of methyl propiolate by arylhydrosilanes gives the α-isomer predominantly (Table 3). Dimethyl(2-thienyl)silane reacts quantitatively at 50°C; the yields of the products for di- and tri-thienyl derivatives are low under the present conditions but reach 95–98% when the temperature is raised to 150°C. The use of $(Ph_3P)_3RhCl$ as catalyst brings about a sharp drop in the reaction yield, while the

TABLE 3

HYDROSILYLATION OF METHYL PROPIOLATE BY ARYLHYDROSILANES $Ar_nSiMe_{3-n}H$ ($H_2PtCl_6 \cdot 6H_2O$, 6 h)

Ar	*n*	Solvent	50°C		150°C	
			Yield (%)	α-/β-*trans*-isomer ratio	Yield (%)	α-/β-*trans*-isomer ratio
	1	–	99.7	69/31	–	–
	2	–	7.5	58/42	95	56/44
	3	–	11	55/45	98	53/47
 [a]	1	–	5	65/35	66	67/33
 [b]	1	hexane	21	53/47	82	56/44
 [b]	1	THF	9.5	55/45	83	67/33
 [b]	1	chloroform	37	56/44	83	63/37
 [b]	1	acetonitrile	5.5	55/45	83	52/48
Ph	1	–	–	–	76	60/40
Ph	2	–	–	–	60	56/44
Ph	3	–	–	–	62	50/50

[a] In the presence of $(Ph_3P)_3RhCl$. [b] 2 ml of solvent was used per 0.0125 *M* initial reagents.

isomer ratio remains unaltered. Hydrosilylation conducted in the solvent (hexane, THF, chloroform, acetonitrile) yields less products.

The reaction of propargyl alcohol with dimethylphenyl- and dimethyl(2-thienyl)-silanes involves, apart from hydrosilylation, dehydrocondensation at the OH group.

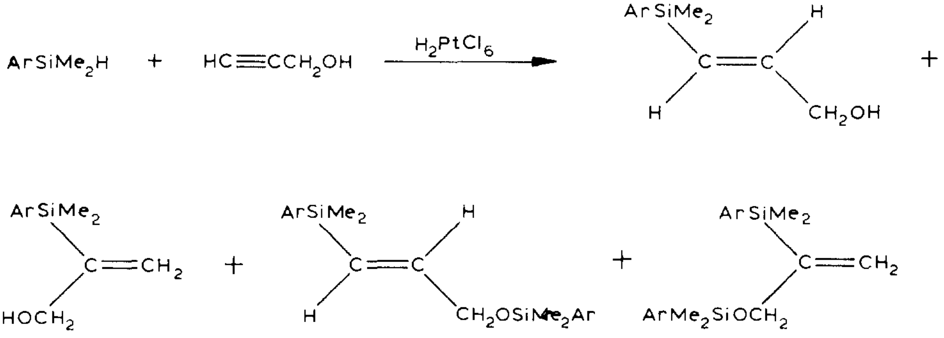
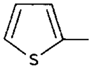
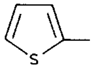
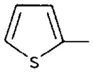
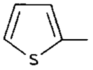
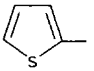


TABLE 4

HYDROSILYLATION OF PROPARGYL ALCOHOL BY ARYLHYDROSILANES $Ar_nSiMe_{3-n}H$ ($H_2PtCl_6 \cdot 6H_2O$, 50°C, 6 h)

Ar	*n*	Yield (%)	*β-trans*	*α*	*β'-trans*	*α'*
 [a]	1	92	42	41	9	8
	1	98	41	39	10	10
 [b]	1	87	47	49	2.5	1.5
	2	85	56	44	–	–
	3	65	60	40	–	–
Ph	1	81	31	27	22	20
Ph	2	75	57	43	–	–
Ph	3	91	65	35	–	–

[a] At 20°C. [b] In the presence of $Co_2(CO)_8$.

At the same time, with diaryl- and triaryl-hydrosilanes only hydrosilylation at the triple bond takes place. The regioselectivity of the reaction rises with increasing number of aromatic substituents in the hydrosilane. This is so both for the hydrosilylation of propargyl alcohol and its methyl ether (Tables 4 and 5). The use of $Co_2(CO)_8$ instead of $H_2PtCl_6 \cdot 6H_2O$ at 50°C only insignificantly affects the total

TABLE 5

HYDROSILYLATION OF PROPARGYL METHYL ETHER BY ARYLHYDROSILANES $Ar_nSiMe_{3-n}H$ ($H_2PtCl_6 \cdot 6H_2O$, 50°C, 6 h)

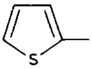
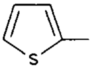
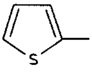
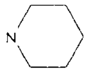
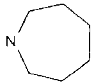
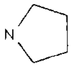
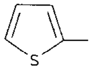
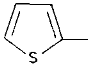
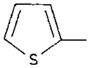
Ar	*n*	Yield	*β-trans*/*α*-isomer ratio
	1	84	61/39
	2	73	63/37
	3	54	64/36
Ph	1	88	56/44
Ph	2	87	68/32
Ph	3	80	74/26

TABLE 6

HYDROSILYLATION OF PROPARGYL AMINES HC≡CCH$_2$X BY ARYLHYDROSILANES Ar$_n$SiMe$_{3-n}$H IN THE PRESENCE OF H$_2$PtCl$_6$·6H$_2$O FOR 6 h (overall yield (*β-trans*/α-isomer ratio))

Ar	*n*	X = 		X = 		X = 		X = NEt$_2$	
		150°C	200°C	150°C	200°C	150°C	200°C	150°C	200°C
	1	99(80/20)	86(85/15)	85(84/16)	65(88/12)	64(84/16)	71(84/16)	90(86/14)	83(84/16)
	2	83(85/15)	85(82/18)	35(86/14)[a]	62(92/8)	35(88/12)[a]	75(85/15)	75(84/16)	70(86/14)
	3	69(92/8)	–	56(100/0)	–	14(92/8)	–	39(81/19)	–
Ph	1	75(83/17)	98(94/6)	70(79/21)	70(79/21)	78(82/18)	96(90/10)	72(80/20)	76(78/22)
Ph	2	55(88/12)	85(81/19)	48(89/11)	64(84/16)	32(92/8)[a]	60(75/25)	10(81/19)	57(80/20)
Ph	3	85(99/1)	–	42(95/5)	–	82(93/7)	–	37(85/15)	–

[a] Heating time 20 h.

yield of the reaction of dimethyl(2-thienyl)silane with propargyl alcohol, whereas the yields of the *β'-trans-* and *α'*-products become lower. When the temperature is decreased to 20°C in the presence of Speier's catalyst the reaction yield is only slightly affected (a decrease from 98 to 92%), the isomer ratio remaining the same.

The overall yield of the products of hydrosilylation of propargyl amines by arylhydrosilanes(Speier's catalyst, 150°C, 6 h) decreases from monoaryl- to diarylsilanes. The amount of *β-trans*-isomer increases with increasing number of aromatic substituents at the silicon atom, but in the case of tri(2-thienyl)silane and *N*-propargylperhydroazepine, the *β-trans*-isomer is the only product formed (Table 6). Among the amines, the highest reactivity is exhibited by *N*-propargylpiperidine, which reacts at 150°C with dimethyl(2-thienyl)silane in the presence of $H_2PtCl_6 \cdot 6H_2O$ (yield: 99%). However, when the hydrosilylation of *N*-propargylpiperidine by dimethyl(2-thienyl)silane is carried out at 20°C for 180 days or at 50°C for 6 h, the respective yields are 9 and 2.6%. By raising the temperature to 200°C, a considerable increase of the yield is attained in the case of inactive amines.

The use of $(Ph_3P)_3RhCl$, $H_2OsCl_6 \cdot 6H_2O$, or $Co_2(CO)_8$ instead of Speier's catalyst is accompanied by an abrupt drop in the reaction yield (Table 7). Depending on the catalyst used, the yields of the hydrosilylation products in the reaction of *N*-propargylpiperidine and dimethyl(2-thienyl)silane decline in the sequence: $H_2PtCl_6 \cdot 6H_2O > (Ph_3P)_3RhCl > H_2OsCl_6 \cdot 6H_2O \geqslant Co_2(CO)_8$.

Only with the rhodium catalyst at 200°C does the yield reach 80%, the *β-trans-* and *α*-isomers being formed along with the *β-cis*-isomer (71/13/16). In the presence of $Co_2(CO)_8$ even at 200°C the reaction yield never exceeds 10%.

For *para*-substituted methyldiphenylhydrosilanes ($H_2PtCl_6 \cdot 6H_2O$, 150°C, 6 h) the overall yield of *N*-propargylpiperidine hydrosilylation depends on the substituent in the aryl ring and diminishes in the order: $F = Me_2N > H > Cl \geqslant Br > Me$. The isomer ratio is not affected so appreciably by the substituent (Table 8).

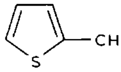
The reactivity of the unsaturated compounds in question reacting with the most active hydrosilane, dimethyl(2-thienyl)silane, lose their activity in the following sequence of substituents at 50°C: COOMe ≈  $\geqslant CH_2OH > Ph >$

TABLE 7

HYDROSILYLATION OF *N*-PROPARGYLPIPERIDINE BY DIMETHYL(2-THIENYL)SILANE IN THE PRESENCE OF VARIOUS CATALYSTS FOR 6 h

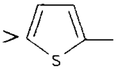
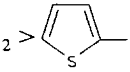
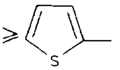
Catalyst [a]	*T* (°C)	Yield (%)	*β-trans*/*α*-isomer ratio
$H_2PtCl_6 \cdot 6H_2O$	150	99	80/20
$H_2PtCl_6 \cdot 6H_2O$	200	86	85/15
$(Ph_3P)_3RhCl$	150	36	89/11
$(Ph_3P)_3RhCl$	200	80	73/13/16 [b]
$H_2OsCl_6 \cdot 6H_2O$	150	10	84/16
$H_2OsCl_6 \cdot 6H_2O$	200	44	85/15
$Co_2(CO)_8$	150	9	67/33
$Co_2(CO)_8$	200	10	78/22

[a] 3.5×10^{-7} *M* catalyst was used per 0.05 *M* of initial reagents. [b] *cis*-Isomer.

TABLE 8

HYDROSILYLATION OF *N*-PROPARGYLPIPERIDINE BY SUBSTITUTED PHENYLHYDROSILANES, $(p\text{-}XC_6H_4)_2SiMeH$ ($H_2PtCl_6 \cdot 6H_2O$, 150°C, 6 h)

X	Yield (%)	*β-trans*/*α*-isomer ratio
H	55	88/12
Me	36	88/12
F	70	91/9
Cl	47	93/7
Br	46	91/9
Me_2N	70	94/6

$CH_2OMe >$  $> CH_2NR_2$; the amount of *β-trans*-isomer declines in the order X: $CH_2NR_2 >$  $CH_2 \geqslant Ph > CH_2OMe > CH_2OH > COOMe \geqslant$  .

Experimental

The initial hydrosilanes were prepared by organomagnesium synthesis [4]; the dimethylphenylsilane and triphenylsilane were purchased from Fluka.

As catalysts, we used 0.1 *M* and 0.05 *M* $H_2PtCl_6 \cdot 6H_2O$ in propan-2-ol as well as $(Ph_3P)_3RhCl$ and $Co_2(CO)_8$ in the solid state (3.5×10^{-7} *M* per 0.01 *M* of the initial reagents).

The hydrosilylation reactions were conducted in Pierce reactors at 50 and 150°C. A mixture of 0.005 *M* hydrosilane and 0.005 *M* acetylene derivative with Speier's catalyst (3.5×10^{-7} *M*) added to it was heated for 6 h. The ratio of isomers was determined on the basis of GLC, ^1H NMR and GC/MS spectra.

The ^1H NMR spectra were recorded with a Bruker WH-90/DS spectrometer (90 MHz) using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Mass spectra were obtained on a Kratos MS-25 GC/MS system (70 eV). Chromatography of the mixtures was done with Model 3700 Varian and Khrom-5 instruments using 1.2 m long columns (inner ϕ3.0 mm) packed with chromosorb W-HP containing 5% OV-17. The temperature of the dispenser and of the flame-ionization detector was 250°C; that of the column rose in the course of operation from 80 to 250°C at 10°/min.

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